

SORBATE AND LEACHATE CHARACTERISTICS OF FLY ASH

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Increased reliance on coal combustion can give rise to significant fly ash storage or disposal problems. Most fly ash is presently used as a low cost material for construction purposes and also as cover material for landfills. Other, more economically advantageous uses for this inexpensive material would be desirable. One such use for fly ash could be to treat ash pond effluent for reuse by power plants as cooling tower makeup water. Another application could be as sorbents of the heavy metals, toxic anions and organic substances commonly found in leachates emanating from landfills. Over the past several years, our laboratory has developed, under EPA Grants R803-717-91 and R803-717-02 a method for the treatment utilizing fly ash alone or in combination with other inexpensive sorbents for the removal of heavy metals, toxic anions and organics from industrial sludge leachates and industrial waste stream effluents. During the course of these investigations, two types of fly ash were repeatedly collected at different times from the same electrostatic precipitator at a coal burning boiler of a large east coast electric utility. These fly ashes exhibited different leaching and sorbent characteristics; i.e. one type produced an acidic leachate while the other leached basic. Although both fly ashes initially leached both cations and anions, the leaching eventually ceased and removal of these species occurred. For example, the fly ash whose effluent was initially acidic leached copper (0.69 micrograms/gram of fly ash) and zinc (0.32 micrograms/grams of fly ash) when this material was placed in a lysimeter and eluted with industrial sludge leachate. After a period of time the leaching ceased and both copper and zinc in the treated effluent were reduced from about 2.5 mg/l and 0.4 mg/l, respectively, to 0.01 mg/l.⁽¹⁾ Since each fly ash type exhibited different sorbent characteristics, a mixture of both types was found to be more effective in the treatment of industrial sludge leachates. Up to this point, the availability of the different types of fly ash from the power plant could not be predicted. One simply had to collect what was available and determine its characteristics by testing. This lack of an adequate supply of fly ashes with the desired sorbent characteristics inhibited the further development of this low cost technology for the treatment of industrial waste effluent and leachate from industrial landfills. Therefore, an investigation was carried out in order to correlate the sorbent and leaching characteristics of fly ash produced with the composition of the coal and the combustion conditions that existed during the production of these fly ashes.

Three different types of coal fired boilers were utilized in this study. One type (A), a dry bottom boiler, was operated with flame temperatures below the ash fusion temperature of the coal ash. The second type (B), a wet bottom boiler, was operated at flame temperatures which exceeded the ash fusion tem-

perature of the coal ash. The third boiler types (C&D), dry bottom tangentially fired boilers, were operated with flame temperatures that were comparable to the ash fusion temperatures of the coal.

Six high fusion coals and five low fusion coals were burned in these three different boiler types under closely monitored conditions. Table 1 gives a listing of these coals by mine name and location.

TABLE 1
COAL BURNED UNDER TEST CONDITIONS

<u>Mine</u>	<u>High Fusion Coal</u>	<u>Location</u>
Militant		Pennsylvania
Deep Hollow		West Virginia
Upshur		West Virginia
Badger		West Virginia
Mine Mouth C		Pennsylvania
Mine Mouth D		Pennsylvania
	<u>Low Fusion Coal</u>	
Wellmore Cactus		Virginia
Wellmore Ackiss		Virginia
Ellsworth		Pennsylvania
Nora		Pennsylvania
Blend		Not known

Table 2 gives the temperature profile observed in the boilers along with the coal, natural gas and oil feed rates when co-fired or relative power outputs when the coal feed rate was unavailable, boiler additive feed rates, percent excess air, ambient air temperature, barometric pressure and power generation level.

During the combustion of the test coal, coal samples were collected at the entrance to each pulverizer just prior to being burned. The collection of fly ash was timed to correspond to the coal being burned. Different size distributions of the fly ash were obtained by the collection of samples from both the front and back row of electrostatic precipitators. The coals and their ashes were analyzed for %C, %S, %SiO₂, %Al₂O₃, %Fe₂O₃, %CaO, %K₂O, %Na₂O, %MgO, ppm of Ti, Cd, Cu, Cr, Pb, Zn, Sn, Ni, Mn, ash content and ash fusion temperatures according to ASTM procedures.

The difference in leaching of Cadmium, Boron, Tin, Molybdenum, Nickel, Lead, Copper, Chromium, Zinc, Manganese and Iron from both the high fusion and low fusion fly ashes in general were found to be dependent upon the differences in trace amounts of these elements present in the fly ash, the differences in the size of the fly ash particles and the differences in boiler temperatures encountered by the fly ashes during their generation.

The differences in the amount an element is leached from the fly ashes was found to be related directly to the concentration in the fly ash for a majority of the elements examined. The differences in the amount of an element present in the high fusion fly ashes in turn is determined by its concentration in the coal and the size of the fly ash particles. The smaller fly ash particles were found to contain greater amounts of specific element than the larger particles. In comparison, the differences in the amount of a specific element found in the low ash fusion was observed to be dependent on its concentration

in the coal, its particle size as well as boiler temperatures. The smaller low fusion fly ash particles and lower boiler temperatures, when compared to the larger particles and higher boiler temperatures, contained the greater amounts of the majority of the above elements.

TABLE 2

Upper Reading Conditions of Coal Fired Boilers

Boiler A Generation Station

Coal	Coal (TPH)	Oil %	Gas (MCF)	Pressure (MM/S)	Excess O ₂ %	Additive Feed Rate		Power	Boiler Temperature (F)		
						LPH-40 Gal/hr	CTRL M Lbs/hr		Flame	Above Basket	Super Heater
Militant	110	0	2900	30.8	5.4	18	25	full	-	-	-
Militant	108	0	400	30.5	8.0	18	25	min.	-	-	-
Militant	102	0	1125	30.5	6.6	18	25	int.	-	-	-
Militant	110	0	3145	30.5	3.9	17.5	25	full	-	-	-
Deep Hollow	140	32	0	29.65	5.4	14	25	full	-	-	-
Deep Hollow	114	0	0	29.65	8.0	14	25	low	-	1450	-
Deep Hollow	142	0	0	29.65	6.8	16	20	int.	-	1550	-
Upshur	198	0	0	29.8	4.7	18	0	full	2470	1590	1565
Badger	188	0	0	29.3	3.1	18	25	full	2550	1750	1440

Boiler B Generation Station

Coal	Relative Power output %	Pressure (mmHg)	% Excess O ₂	Additive Feed Rates		#11 Boiler Temp. Above Flame			#12 Reheater Temp. Above Flame		
				LPA-40 gal/hr	Control M lbs/hr	Flame	Basket	Arch	Flame	Basket	Arch
Wellmore Cactus #1	89	-	3.8	32	0	3150	1620	2080	3150	1530	1480
Wellmore Cactus #2	100	27.8	3.3	28	0	3125	1400	1680	2970	1400	1320
Blend	95	27.8	3.4	28	0	3100	1815	2250	3100	1737	1835
Ellsworth	98	27.7	3.5	0	0	3100	1815	2240	3100	1740	1820
Wellmore	94	27.8		16	0	3050	1900	2180	2950	1725	1500
Ackiss	50	27.8	5.0	16	0	2870	1590	1780	2950	1620	1500
Nora	97	-	3.5	20	0	3100	1850	2175	3250	1700	1700

Boiler C and Boiler D Generation Station

Coal	Coal (TPH)	Pressure (mmHg)	% Excess O ₂	Additive Feed Rate		Power	Boiler Temperature Above Flame		
				LPA-40 gal/hr	Control M lbs/hr		Flame	Basket	Arch
Boiler C	313	-	4.2	0	0	full	-	2600	-
Boiler D	303	-	4.7	0	0	full	2650	2700	2700

There appears to be some correlation between the differences in trace element leaching observed for the fly ashes and the concentration of these elements at the surface of the fly ash particles provided that greater than 50% of the element is concentrated at the surface. Hansen and Fischer ⁽²⁾ have shown that the major portion of the Cd, Cu, Zn, Cr, Pb, and Mo present in the fly ash particles are concentrated at the surface of the fly ash particles. Our results reveal that the difference in leaching of the Cd, Cu, Zn, Cr, Pb and Mo by a majority of the fly ashes can be correlated with the differences in the amounts of those elements present in the fly ashes. However, when the trace elements are not concentrated at the surface, as was reported by Hansen and Fischer to be the case for Ni and Fe ⁽²⁾, our results indicate no correlation between the difference in leaching by the fusion fly ashes and the differences in the amounts of these elements present in these fly ashes.

The exceptions to the above correlations is Mn. Although, the concentration of Mn at the surface of the fly ash particles was reported by Hansen and Fischer to be less than 50%, our results show that most of the differences in leaching exhibited by the Blend, Wellmore Cactus #1, Militant, Deep Hollow and Wellmore Ackiss fly ashes can be correlated with the differences in the amount of manganese present in these fly ashes.

Differences in the leaching of the above elements as they relate to particle size and boiler temperatures is explained as follows. A comparison of the elements leached from small fly ash particles and large fly ash produced from the same coal under the same boiler conditions show the smaller particles in general leach greater quantities of the above elements than the larger particles. If the distribution of leachate elements within the different phases present in the fly ash are the same, the smaller particles would expose a greater leachable surface area.

Boiler temperatures probably influence the leaching characters of the fly ashes by fixation of the leachable elements. The different leaching results obtained with the low fusion fly ashes produced from the same coal at the same time indicated that operation of the boiler at temperatures above the ash fusion temperatures, along with the ash remaining in the fused state for longer lengths of time can reduce the leaching exhibited by the fly ashes. Apparently, these temperatures, lead to some fixation of these elements into the non-soluble portion of the fly ash. The leaching results suggest that the leachable elements are contained to some extent within a water soluble component located at the surface of the ash which is eventually removed when the fly ash is brought in contact with the aqueous ash pond effluent. The leachable amounts of each element can be in general related to 1) the amount of this element present in the fly ash (provided that a major portion to the element is located at the surface), 2) the surface area of the fly ash particles and 3) the boiler temperature encountered by the fly ashes during their formation.

Three separate ash pond samples were used to evaluate the effectiveness of the fly ash in treating fly ash pond effluent. Analysis of these ash pond samples are presented in Table 3.

The results show that fly ash can be used for treatment of Cd, B, Sn, Mo, Ni, Pb, C, Cu, Zn, Mn, Fe, As and organics in these ash pond effluents. Removals of greater than 75 percent were achieved for all of the above elements with the exception of Boron and Molybdenum where removals of only 21% and 43%, respectively were obtained. For example, Figure 1 shows that the concentration of lead remaining in the treated ash pond sample remained below detectable levels with no indication of breakthrough even after passing 36 liters of ash pond sample through the fly ash generated from the Nora coals. These removals

were achieved even though the concentration of lead in the ash pond sample was increased to 3.0 mg/l (see dotted line in Fig.1). The maximum allowable primary drinking standard for lead is 0.05 mg/l. The exceptional removal of lead does not appear to be due to precipitation since the concentration of lead in the ash pond sample was kept below the maximum solubility of the lead as measured as a function of pH (See Fig. 2). Also, the pH measured in the treated ash pond effluent ranged from an alkaline value of 10 down to an acidic value of 6 during the removal of lead from 36 liters of ash pond sample. (See Fig. 3).

TABLE 3

Elemental Concentration of Actual Ash Pond Effluent Used
In Fly Ash Sorbate Characterization

Element	Sample A mg/l	Sample B mg/l	Sample C mg/l
Cadmium	N.D.*	N.D.*	0.02
Boron	3.30	3.30	2.80
Tin	0.90	2.07	1.01
Molybdenum	3.0	2.70	0.41
Nickel	0.26	0.11	0.09
Lead	1.80	0.35	0.62
Copper	.01	0.01	0.09
Chromium	.48	0.18	0.09
Zinc	.16	0.06	1.48
Manganese	.24	0.24	0.40
Iron	0.22	0.05	0.10
Arsenic	0.16	0.15	0.13

*N.D. - below measurable limits

The general sorbate characteristics of the fly ashes are favored by low ash fusion temperatures, combustion temperatures that favor the fusion of the fly ash during formation and the time that the fly ashes remain in the fused state. No correlation could be established between the sorbate characteristic of the fly ashes and their bulk major, minor and trace elemental compositions nor with their major and minor elemental surface compositions. Also, no correlation could be established between the treatment achieved with the fly ashes and particle size of the fly ash particles. Only the carbon content of the fly ash could be related to its organic removal properties.

The sorbate capacities of the fly ashes, identified in this investigation to provide the best treatment, average about 80 ug/gm for the Cadmium, Copper and Zinc, 3.4 ug/gm for Arsenic and 700 ug/gm for the organics. However, the sorbate capacity for Arsenic may be increased with further washing of the fly ashes.

These capacities were found to be independent of pH in the range from about 6 to 10. Also, the removals of Cadmium, Copper, Lead and Zinc were observed to be independent of their inlet concentrations in the ranges from 0.52 mg/l to 2.0 mg/l, 0.52 mg/l to 3.5 mg/l, 0.30 mg/l to 3.0 mg/l and 0.56 mg/l to 4.0 mg/l, respectively.

Greater than 75 percent removals of the Cadmium, Copper and Zinc present in the ash pond samples were achieved within a 15 minute contact time between the fly ash and the sample. The results indicate that removal of the above elements in ash pond effluent can be achieved with the same fly ash that origi-

nally leached these elements. The washed fly ash was observed to have a significant excess of sorbative capacity beyond that required to treat the elements originally leached from the fly ash.

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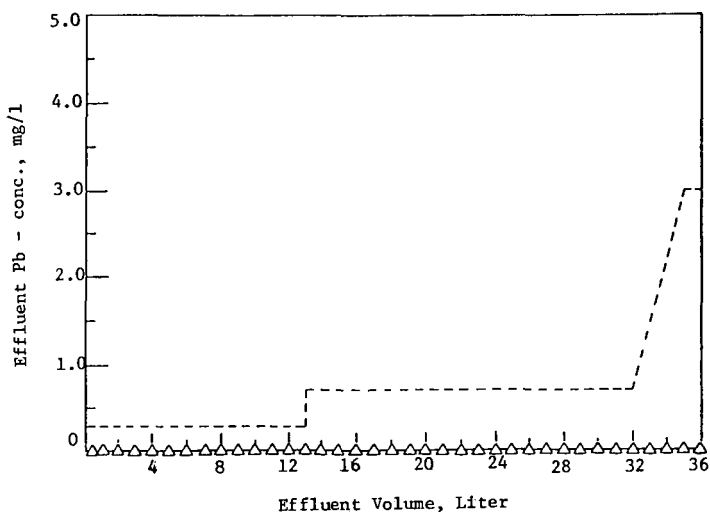


Fig. 1 Concentration of Lead Remaining After Treatment with Nora Fly Ash, 500 grams

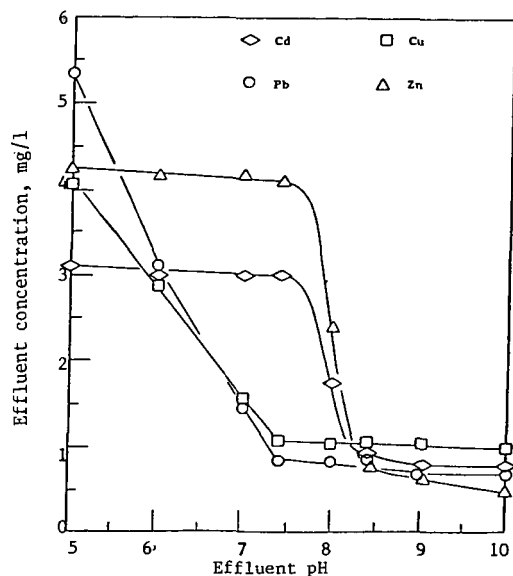


Fig. 2. pH Effect on Cadmium, Copper, Lead and Zinc Solubility in Ash Pond Sample D.

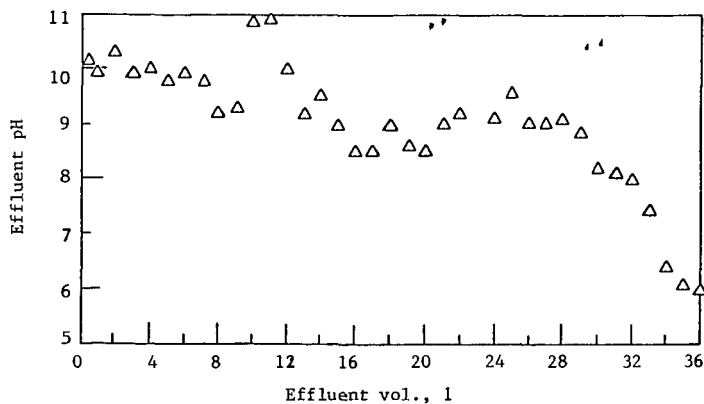


Figure 3. pH of Treated Ash Pond Sample Using Nora Fly Ash